Attorney Docket No. 8793-52026 **PATENT**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE THE PATENT APPLICATION OF: Bellaiche, L., et al.

Appl. No.: 10/632,740 Group Art Unit: 1755

Filed: 08/01/2003 Examiner: Koslow, C.

For: Enhanced Electromechanical Properties in Atomically-Ordered Ferroelectric Alloys

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER RULE 131

1. This declaration is to establish completion of the invention in this application in the United States, at a date prior to December 2001, that is the effective date of the prior art publication (the Thesis by A. George) that was cited by the examiner in the office action of August 31, 2004.

2. The persons making this declaration are the inventors.

Facts and Documentary Evidence

3. To establish the date of completion of the invention of this application, the following attached documents are submitted as evidence:

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4. The examiner's attention is particularly directed to the last full paragraph on page 56 of the document cited above. This paragraph is quoted in its entirety as follows:

"We also numerically found (results not shown here) that continuously increasing ν from 0 to 0.44 leads to a continuous decrease of the orthorhombic-to-monoclinic transition temperature from 373 K to 0 K. As a result, the temperature at which d_{34} and χ_{33} both peak depends on the value of the ν parameter. This dependency could lead to the development of devices with electromechanical performances optimized for any temperature between 373 K and 0 K."

This paragraph also appears at paragraph **[0018]** of the specification.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that the statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section

1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Jorge Iniguez

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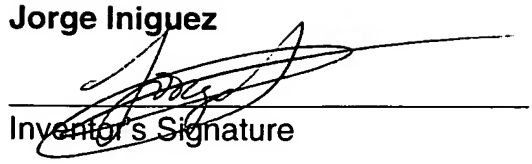

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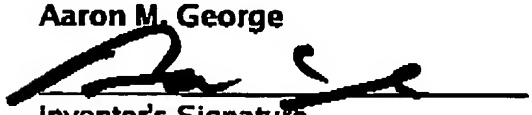

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Anomalous properties in ferroelectrics induced by atomic ordering

A. M. George, Jorge Íñiguez & L. Bellaiche

Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA

Complex insulating perovskite alloys are of considerable technological interest because of their large dielectric and piezoelectric responses. Examples of such alloys include $(Ba_{1-x}Sr_x)TiO_3$, which has emerged as a leading candidate dielectric material for the memory-cell capacitors in dynamic random access memories[1]; and $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), which is widely used in transducers and actuators[2]. The rich variety of structural phases that these alloys can exhibit, and the challenge of relating their anomalous properties to the microscopic structure, make them attractive from a fundamental point of view. Theoretical investigations of modifications to the atomic ordering of these alloys suggest the existence of further unexpected structural properties[3] and hold promise for the development of new functional materials with improved electromechanical properties. Here we report *ab initio* calculations that show that a certain class of atomic rearrangement should lead simultaneously to large electromechanical responses and to unusual structural phases in a given class of perovskite alloys. Our simulations also reveal the microscopic mechanism responsible for these anomalies.

The class of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT) perovskite ferroelectric alloys have been reported[4] to show remarkably large piezoelectric constants around $2{,}000\,pC\,N^{-1}$. These materials thus promise improvements in the resolution and range of ultrasonic and sonar listening devices[5]. Perovskite $A(B'B''\ldots)O_3$ alloys are also of great interest, as demonstrated by the discovery of an unexpected monoclinic phase[6] in $Pb(Zr_{1-x}Ti_x)O_3$. These two findings have led to a search for materials with even larger electromechanical response and/or currently unobserved phases. In particular, if a mechanism can be found that occurs in a large number of ferroelectric alloys, markedly enhances the piezoelectricity and the dielectric responses, and leads to unexpected structural features, that mechanism is likely to have large technological and fundamental implications. Here we report that such a mechanism exists and simply consists in rearranging in a certain way the atoms in a heterovalent alloy (that is, an alloy made of atoms belonging to different columns of the periodic table). More precisely, we predict that materials made of the sequences $Pb(Sc^{3+}_{0.5+r}Nb^{5+}_{0.5-r})O_3$/$Pb(Sc^{3+}_{0.5}Nb^{5+}_{0.5})O_3$/$Pb(Sc^{3+}_{0.5-r}Nb^{5+}_{0.5+r})O_3$/$Pb(Sc^{3+}_{0.5}Nb^{5+}_{0.5})O_3$ along the [001] direction should show very large electromechanical responses,

and unusual monoclinic and orthorhombic phases for some values of the ν parameter. The analysis of our results points to the different valence of the B atoms (Sc and Nb) as the main reason for the existence of these anomalous properties.

Here, we use the numerical scheme proposed in refs 7 and 8, which consists of constructing an effective hamiltonian for the alloy from first-principles calculations, to predict the properties of $Pb(Sc_{1-x}Nb_x)O_3$ (PSN) structures. This effective hamiltonian[7,8] contains a local-mode self-energy (expanded in even-order terms up to fourth order of the phonon local soft modes), a long-range dipole–dipole interaction, a short-range interaction between soft modes (quadratic order of the soft modes), an elastic energy (expanded to second order of the strain variables), and an interaction between the local modes and local strain (second order of the soft modes and first order in strain). It also contains an energy term describing the effects of the atomic configuration on the phonon local soft modes (which are directly related to the electrical polarization) which can be written as

$$\Delta E = -\sum_i Z^* \mathbf{u}_i \cdot \left[\sum_j -\sigma_j S_{ji} \hat{\mathbf{e}}_{ji} \right] \quad (1)$$

where i runs over all the cells and j runs over the three nearest-neighbour shells of cell i. Here $\mathbf{u}_i$ is the local soft mode in cell i, Z^* is the Born effective charge associated with the local soft modes, and $\hat{\mathbf{e}}_{ji}$ is the unit vector joining the B site j to the B site i. The variables $\{\sigma_j\}$ characterize the atomic configuration: $\sigma_j = +1$ (-1) indicates that there is an Nb (Sc) ion in cell j. S_{ji} is an alloy-related parameter that only depends on the distance between the B sites i and j, and is derived from first-principles calculations[9–12] on small cells. Equation (1) indicates that ΔE can be viewed as the interaction energy between the dipole moment $Z^*\mathbf{u}_i$ associated with the site i and an internal electric field $\Sigma_j - \sigma_j S_{ji} \hat{\mathbf{e}}_{ji}$ induced by the B ions of sites j on the site i. Moreover, we numerically find that the S_{ji} parameters all have negative signs. As a result, the radial electric field $-\sigma_j S_{ji} \hat{\mathbf{e}}_{ji}$ acting on site i and induced by a Sc^{3+} (Nb^{5+}) ion sitting on site j is directed from the site i to the site j (respectively, from site j to site i). This is consistent with an electrostatic picture of PSN since Sc (Nb) ions are negatively (positively) charged with respect to the average B-ion valence of 4+. The effective hamiltonian approach yields good agreement with direct first-principles results in PZT and PSN alloys[7,8]. Previous works (see refs 7–8) have found that a linear rescaling of the simulation temperature often leads to good agreement with experiment. Adopting this approach again here, our temperatures are rescaled down by a factor of 2.5 so that the theoretical Curie temperature in disordered PSN is forced to match the experimental value[13]. The need for such rescaling may be due to higher perturbative terms or the rotation of the oxygen octahedra, neglected in our effective model of PSN.

Here, we use the total energy of our alloy effective hamiltonian in Monte Carlo simulations to calculate finite-temperature properties of some selected $Pb(Sc_{1-x}Nb_x)O_3$ structures. We consider structures with the following sequence of four B-planes along the [001] direction (Fig. 1): a niobium-poor plane for which $x = 0.5 - \nu$, a second plane made of 50% scandium and 50% niobium ($x = 0.5$), a niobium-rich plane with $x = 0.5 + \nu$, and a fourth plane similar to the second one. The B atoms are randomly distributed within each of these four planes. The studied structures only differ in the value of the parameter ν, which is allowed to vary from zero (in the case of the disordered PSN alloy) to 0.5 (in the case in which the first plane is entirely made of Sc atoms and the third plane is fully occupied by Nb atoms). We use $12 \times 12 \times 12$ supercells, implying that the sequence of the four different B(001) planes is repeated three times, to get well converged results[7,8].

Figure 2a shows the cartesian coordinates (u_x, u_y and u_z)—along

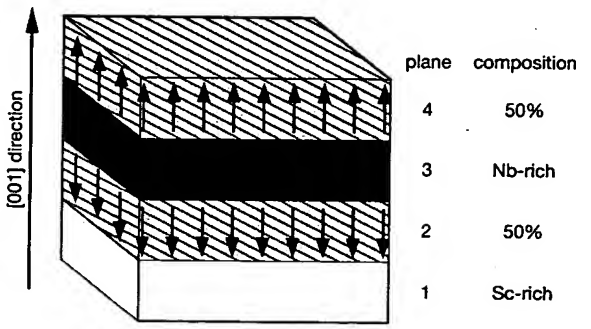

Figure 1 Schematic representation of the ferroelectric structures considered here. The materials are $Pb(Sc^{3+}_{0.5+\nu}Nb^{5+}_{0.5-\nu})O_3/Pb(Sc^{3+}_{0.5}Nb^{5+}_{0.5})O_3/Pb(Sc^{3+}_{0.5-\nu}Nb^{5+}_{0.5+\nu})O_3/Pb(Sc^{3+}_{0.5}Nb^{5+}_{0.5})O_3$ structures. The internal electric fields acting on the four B planes are indicated by arrows.

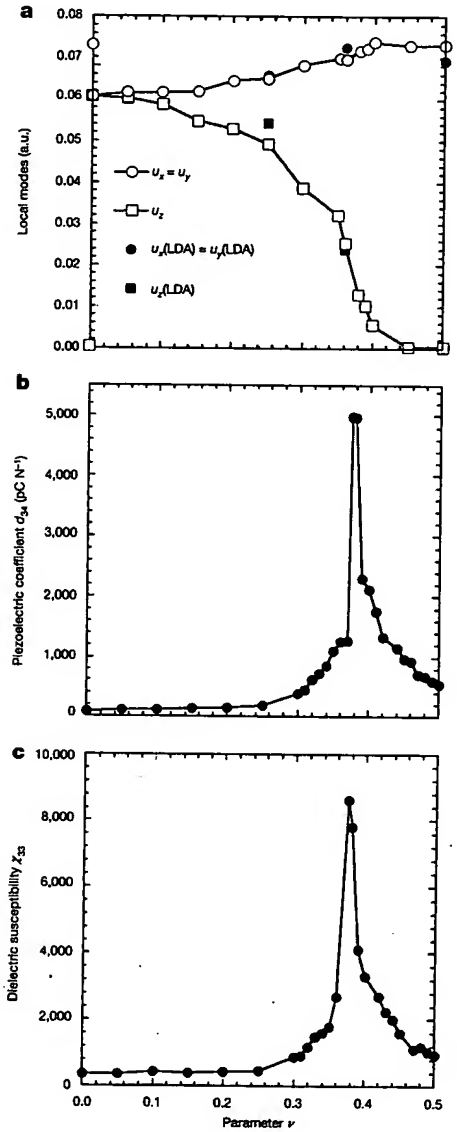

Figure 2 Properties of the studied structures as a function of the ν parameter at 20 K. **a**, Average cartesian coordinates u_x, u_y and u_z of the local mode; **b**, the d_{34} piezoelectric coefficient; **c**, the χ_{33} dielectric susceptibility. The filled symbols in **a** represent the cartesian coordinates u_x(LDA), u_y(LDA) and u_z(LDA) of the local modes predicted by direct first-principles calculations made using the local density approximation[9–12]. a.u., arbitrary units.

the [100], [010] and [001] directions, respectively—of the supercell average of the local mode vectors as a function of this parameter ν at 20 K. The structure for which ν is null has $u_x = u_y = u_z \neq 0$. This characterizes a ferroelectric rhombohedral structure in which the polarization is directed along the pseudo-cubic [111] direction, consistent with experiments on disordered PSN samples[13]. Interestingly, increasing ν results in a strong decrease of u_z whereas u_x and u_y slowly increase and remain equal to each other. This behaviour corresponds to a ferroelectric phase of monoclinic symmetry for which the polarization lies between the [111] and [110] directions (the one denoted M_B in ref. 14). When ν is larger than 0.44, u_z becomes null and u_x and u_y reach their maximum value, indicating that the resulting phase is now of orthorhombic symmetry with a polarization lying along the [110] direction. Increasing the parameter ν thus leads to three different ground states and to a continuous rotation of the electrical polarization. To our knowledge, the predicted monoclinic M_B ground state has never been observed in any perovskite material without the aid of external stress or electric field. Similarly, we are not aware of any studies pointing to an orthorhombic ground state in PSN. The existence of these monoclinic and orthorhombic phases is due to the energy term described in equation (1). Figure 2a also shows the predictions of local density approximation[9–11] calculations performed on 20-atom supercells mimicking the structures corresponding to $\nu = 0.25$, $\nu = 0.36$ and $\nu = 0.50$. In these supercells, each B(001) plane is represented by a virtual atom corresponding to the composition in this plane[12,15]. The direct first-principles calculations agree with the predictions of our effective hamiltonian approach, thus further supporting the existence of these unusual monoclinic and orthorhombic phases.

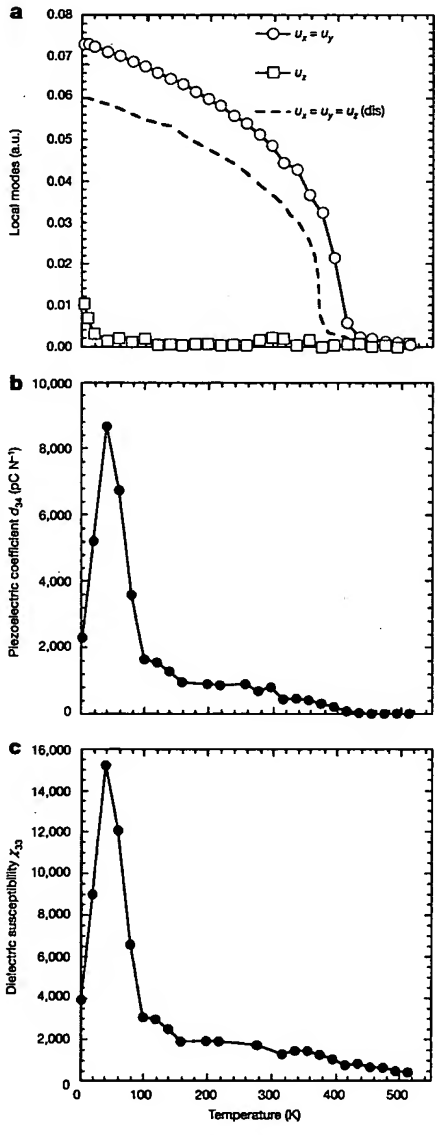

Figure 3 Properties of the structure associated with $\nu = 0.375$ as a function of temperature. Panels **a**, **b** and **c** display the same property as the corresponding panels of Fig. 2. Dashed line in **a** shows one of the three cartesian coordinates (u_x) of the local mode in disordered (dis) PSN (the two other cartesian coordinates are nearly identical to the one displayed, and are omitted for clarity).

Figure 2b summarizes the effects of the parameter ν on piezoelectricity and Fig. 2c the effects on dielectric response at 20 K. We found that the electromechanical coefficients most affected by the atomic ordering are the shear d_{34} piezoelectric coefficient and the χ_{33} dielectric susceptibility, when expressing both piezoelectric and dielectric tensors in the orthonormal basis formed by $\mathbf{a}_1 = [100]$, $\mathbf{a}_2 = [010]$ and $\mathbf{a}_3 = [001]$. More precisely, Fig. 2b shows that d_{34} reaches a peak and remains at large values for a broad range of ν centred around the monoclinic-to-orthorhombic phase transition. Figure 2c demonstrates that the studied atomic ordering simultaneously results in a large dielectric response, as χ_{33} achieves values above 1,000 at 20 K when ν is greater than 0.3.

We now investigate the finite-temperature properties of a structure showing one of the largest electromechanical responses at 20 K. More precisely, we focus on the structure for which $\nu = 0.375$. Figure 3a shows the cartesian coordinates of the supercell average of the local mode vectors as a function of temperature for this structure, and compares them with those of the disordered PSN material. Each coordinate of the local mode in each structure is close to zero at high temperature, characterizing a paraelectric phase. At a temperature close to 373 K, the disordered material undergoes a transition from a paraelectric cubic phase to a ferroelectric rhombohedral structure (for which $u_x = u_y = u_z$), consistent with experiments[13]. The disordered PSN material then remains in the rhombohedral phase for lower temperature. On the other hand, the modulated structure with $\nu = 0.375$ adopts three different phases: a paraelectric tetragonal phase induced by atomic ordering (for which $u_x = u_y = u_z = 0$) at high temperature, an orthorhombic ferroelectric phase ($u_x = u_y \neq 0$ and $u_z = 0$) for temperature between 400 K and 40 K, and the monoclinic ferroelectric M_B phase ($u_x = u_y > u_z$, with $u_z \neq 0$) for temperature lower than 40 K. As shown in Fig. 3b and c, the existence of the orthorhombic-to-monoclinic phase transition results in huge electromechanical responses peaking around this transition and occurring over a broad range of temperature. In fact, d_{34} and χ_{33} are greater than 1,500 pC N^{-1} and 3,000, respectively, for any temperature lower than 100 K.

We also numerically found (results not shown here) that continuously increasing ν from 0 to 0.44 leads to a continuous decrease of the orthorhombic-to-monoclinic transition temperature from 373 K to 0 K. As a result, the temperature at which d_{34} and χ_{33} both peak depends on the value of the ν parameter. This dependency could lead to the development of devices with electromechanical performances optimized for any temperature between 373 K and 0 K.

The intriguing results of Figs 2 and 3 can be understood by means of equation (1). The internal electric field $\Sigma_j - \sigma_j S_{ji} \hat{\mathbf{e}}_{ji}$ acting on each B(001) plane is represented in Fig. 1. The atoms in plane 2 feel an internal electric field oriented along the [00$\bar{1}$] direction whereas the atoms in plane 4 feel an internal electric field along the [001] direction. It is straightforward to demonstrate that the magnitude of these fields is linearly dependent on the parameter ν. (These features can be understood qualitatively by simple short-range electrostatic considerations: the difference of valence between Sc and Nb atoms leads to charged B(001) planes with ionic charges

linearly dependent on ν. When electrostatic interactions up to the third-neighbour shells are included, these charged planes generate internal electric fields whose directions are those of Fig. 1 and whose magnitudes are linearly dependent on ν.) Increasing ν thus results in stronger internal fields with opposite directions. These strong opposite fields tend to suppress the polarization's component along the direction of compositional modulation. As a result, u_z becomes smaller than u_x and u_y. The studied structures with intermediate values of ν thus first undergo a paraelectric-to-orthorhombic ferroelectric transition at high temperature before adopting the monoclinic M_B phase for ground state. The modulated structures with the largest values of ν have the strongest internal electric fields, which annihilate u_z at any temperature. Consequently, such structures never reach the monoclinic phase and instead adopt the orthorhombic phase for ground state. The large values of d_{34} and χ_{33} shown in Figs 2 and 3 simply reflect the considerable change of u_z when some parameters are slightly modified (ν at a fixed temperature, or T for a fixed value of ν), especially for structures at the borderline between the monoclinic and orthorhombic phases. In other words, the large electromechanical responses are consistent with the ease of rotating the polarization[7,16]. We have shown here results for the thinnest possible structures. For larger structures, with thicker layers, the 'unusual' electromechanical responses will be smaller due to smaller internal electric fields.

On the basis of the electrostatic considerations discussed above, we expect that any alloy made of heterovalent atoms and with a rhombohedral ground state in its disordered form should have the structural, piezoelectric and dielectric anomalies displayed in Figs 2 and 3, when the atomic ordering along the [001] direction is adjusted in a certain way. The atomically ordered structures discussed here could be grown by means of a pulse laser deposition technique[17] or by using molecular beam epitaxy. □

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